THE CHEMCHAR PROCESS
FOR HAZARDOUS WASTE TREATMENT

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by

AUDREY ELIZABETH MCGOWIN

Professor Stanley E. Manahan   Dissertation Supervisor

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CHAPTER 1

REVERSE-BURN GASIFICATION: AN ALTERNATIVE METHOD FOR THERMAL TREATMENT OF HAZARDOUS WASTE

INTRODUCTION

Along with increasing public support for sound environmental practices, the implementation of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (Superfund) have forced industry and government to adopt waste management policies that emphasize the reduction of waste and waste treatment to destroy toxic components. The land ban program, started up under RCRA, prohibits the land disposal from several hundred waste streams unless they have been treated with the best technology available to destroy their toxic constituents. Under the supervision of the Environmental Protection Agency (EPA), the waste stream is to be treated so that prior to land disposal the toxicity, mobility, and volume is reduced to the maximum extent achievable. Currently, incineration and stabilization are the most widely utilized technologies for this purpose.[1,2] The practice of treatment prior to land disposal has also caused a tremendous increase in waste disposal costs resulting from increased handling of the waste and energy requirements for the various methods of waste treatment employed. Thermal methods of waste destruction, incineration being the most popular, are quite energy intensive and are a method of choice for cleaning up abandoned and uncontrolled waste sites under Superfund.

There are a variety of thermal methods available for the treatment of hazardous waste.[3,2,4,5,6] The method chosen depends on the form and content of the waste. Waste material can be in the from of a liquid, a solid, or a sludge. A waste may be composed of

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primarily one component—for example, a waste organic solvent—or contain complex mixtures of organics and inorganics such as cyanide, arsenic, or heavy metals. Wastewater containing organic and inorganic compounds must be treated for removal of hazardous contaminants before being discharged. The term "mixed waste" is used for waste containing mixtures of organics with radioactive waste. The objective of thermal treatment of waste is to destroy the organic portion of the waste, retain the inorganic portion, and minimize the production or release of toxic by-products.

THERMAL METHODS FOR HAZARDOUS WASTE TREATMENT

Incineration

There are four types of incineration devices in general use; liquid injection, rotary kiln, fixed-hearth, and fluidized bed.[7] The incinerator design chosen depends on the physical form and other characteristics of the waste to be treated.

Liquid injection incinerators are employed to treat pumpable liquid waste. The device consists of a refractory-lined cylinder containing one or more burners through which wastes are injected. The waste is atomized mechanically, or by air or steam, into fine droplets that are burned in suspension. Sufficient residence time of the droplet is required for the three stages of combustion to occur; heating, volatilization, and oxidation. If the waste is combustible, it may require no additional fuel. Aqueous wastes and wastes with low energy value can be incinerated by this method if auxiliary fuel is added. Often organic waste can be used as auxiliary fuel.

The atomization nozzle is critical to the operation of the liquid injection incinerator. Its function is to break up the liquid into fine droplets, place the liquid droplets in a specific region of the furnace for optimum destruction, and control the rate of introduction of waste into the furnace. The higher the viscosity of the liquid, the more difficult it is to pump, atomize, and burn. Atomizers are subject to erosion and blockage.

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Rotary kiln incinerators are those in which the primary combustion chamber is a refractory-lined cylinder that rotates. An afterburner is added downstream from the kiln to complete destruction of vaporized waste. Solid waste, sludges, and liquid wastes may be treated by incineration in a rotary kiln. Good mixing is achieved with a loading of 5 to 10 % of the internal volume of the cylinder unless there are extremes in particle size. Large amounts of small particles can collect in a "cold kidney" which is less pervious to reacting gases. Another disadvantage is the need to operate under negative pressure to prevent leaking.

Multiple-hearth incinerators can be used to treat liquid, sludge, or solid wastes. Originally developed for ore roasting early in the century, it was easily adapted for sludge incineration. Liquid and solid wastes can be mixed and fed into the system. The multiple-hearth furnace is a vertical structure made of a steel shell, lined internally with refractory. Sludge is fed by gravity at the top or from the side with a screw-type feeder. Inside is a series of circular refractory hearths, with a large circular opening in the center, positioned horizontally with space between them. A vertical shaft at the center of the furnace has rabble arms attached which wipe the sludge across each hearth. Teeth in the rabble arm move the sludge to the center or the outer edge of the hearth where the sludge drops through openings to the next lower hearth. Air is introduced at the bottom of the furnace and off-gas exits the top. The product of the multiple-hearth furnace is ash, 10 to 20 % of which exits with the off-gas and must be recovered. It must be fixed into a leach-resistant solid prior to disposal if it contains hazardous inorganic constituents.

The multiple-hearth furnace is operated at a negative pressure, or draft. Numerous inlets and outlets to the system prevent it from being air-tight; however, leakage under these conditions will be into the system. If the draft is not maintained, emission of potentially dangerous hot gases from the leak points will occur.

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Fluidized-bed incinerators contain a bed of granular solid (usually sand) into which air is introduced through a tuyere plate to create a high degree of turbulence. The undulation created in the top of the bed gives it the appearance of a fluid. Liquids and sludges with solids up to 1/2 inch in diameter can be injected directly into the fluidized bed and macerated solid waste can be fed in just above the bed, however, above-bed feeding can result in incomplete combustion and particulate carry-over. Excellent mixing of the waste and oxidant is achieved in the fluidized-bed incinerator. As with the multiple-hearth furnace, a large portion of the ash produced exits the furnace with the off-gas and must be removed.

Recently, there has been a significant increase in the use of high-energy-value hazardous waste as a fuel source in cement kilns and industrial boilers.[4] Texaco has reported the conversion of large volumes of waste material (tank bottoms sludge) into synthesis gas in the Texaco Gasification Process. The waste sludge was gasified along with with a coal slurry.[8]

Although incineration of hazardous wastes has many advantages, some materials cannot be treated by incineration. Non-combustible soils or wastes containing excessive amounts of water are not incinerable. Supplemental fuel must often be added to maintain the appropriate operating temperature. Also, incineration requires expensive equipment and extensive treatment of the off-gas.

The primary products from combustion are carbon dioxide, water, and ash. Small quantities of a multitude of other products can form. Guidelines set by the EPA must be met by incineration facilities before obtaining operating permits. They must demonstrate that at least a 99.99 % destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) can be achieved (99.9999 % DRE for dioxin and furan containing wastes). If HCl stack emissions are greater than 4 lb/hr, at least 99 % of HCl in the exhaust gas must be removed. Particulate emissions are limited to 0.08 grains/dry

standard cubic foot (dscf) corrected to 7 % oxygen in the stack gas (5.2 mg/ft^3).

Metals such as arsenic, barium, beryllium, chromium, cadmium, lead, mercury, nickel, selenium, and zinc are present in many hazardous wastes. Incineration changes the form of metals in the waste stream but will not destroy them. Metals present in waste streams which are incinerated are typically retained in the ash or emitted in combustion gases as particles rather than vapors. Mercury and selenium tend to be released into the atmosphere in the stack gases.[7]

Products of incomplete combustion (PICs) can be emitted. PICs are organic compounds which are present in the emissions from incineration, which are not present in detectable amounts in the waste feed, fuel, or air fed into the incinerator. PICs can result from incomplete combustion of the original POHCs or they can be created in the combustion zone and downstream as a product of radical-molecule reactions of partially destroyed organics. Hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs)[9] often form during the combustion of chlorinated organic compounds.

Ash residue is generated in waste facilities which incinerate waste containing significant amounts of ash or halogens. The ash often contains heavy metals and undestroyed organic material and is classified as a hazardous waste. Fixation/solidification of the ash is usually necessary prior to disposal to prevent leaching.

Pyrolysis

Pyrolysis is the chemical decomposition or reaction that occurs when material is heated in the absence of oxygen. Solid, sludge, or liquid carbonaceous materials are converted to gases and solid residue. Two steps are used in the pyrolysis of hazardous wastes. First, the waste is heated at 425 to 760 °C to separate the volatile components from non-volatile char and ash. Second, the volatilized fraction is burned under controlled conditions to

optimize destruction of the hazardous components. The solid pyrolyzed residue may still be toxic and must be tested before disposal and further treated if necessary. Pyrolysis requires less particulate emission control than incineration and recovery of vapors and constituents in the residue is sometimes possible. Emission of metals is also greatly reduced. The pyrolysis process is quite energy intensive.

Wet Air Oxidation

Wet air oxidation (WAO) is the aqueous phase oxidation of dissolved or suspended organics at elevated temperature and pressure. Air, or other oxygen-containing gas is bubbled through the heated aqueous solution (175-340 °C) with the process pressure maintained between 300 and 3000 psi to prevent evaporation. The high pressure allows a high concentration of oxygen to be dissolved and reactions occur due to the increased temperature. Gases are removed during the process and hydrocarbons in the gas can be removed by adsorption, wet scrubbing, or afterburning. The oxidized liquid product may require additional treatment such as metal precipitation. The process is designed for treatment of dilute aqueous wastes which cannot be incinerated economically or are too toxic (CN^--containing, etc.) for biological treatment methods.

Plasma Systems

Plasma systems use a plasma-arc to create extremely high temperatures (10,000 °C) to destroy highly toxic wastes. At these temperatures, refractory compounds are readily destroyed. When applied to waste disposal, the plasma arc is considered to be an energy transfer device. The plasma is generated by electrical discharge through a gas causing ionization of the gas. Waste liquids or gases injected into the plasma are destroyed as plasma energy is used to break apart molecules into their constituent atoms. Another way to use plasmas for waste destruction is by indirect heating.[10] The plasma is used as a secondary heat source to create a molten bath of metal or soil which in turn heats and decontaminates the waste. The use of plasmas is only necessary in special cases. To use it

for routine waste treatment would be expensive overkill.

REVERSE-BURN GASIFICATION FOR HAZARDOUS WASTE TREATMENT

The ChemChar Process

The ChemChar Process is a unique new method for the thermal treatment of hazardous waste. Wastes of various forms can be treated including solids, liquids, sludges, and soils. Organic constituents of the waste are destroyed by conversion to a combustible gas. The product is a dry, inert, carbonaceous solid which is either non-hazardous or can be readily mixed with cement to prevent leaching of radioactive, toxic, or heavy metal constituents which are retained in the char residue or ash. In this way, the ChemChar Process can be a very effective method for treating mixed wastes such as heavy metal sludges and organic waste containing radioactive metals. Figure 1-1 is a flow diagram showing the steps of the ChemChar Process followed by a more detailed description of each step.
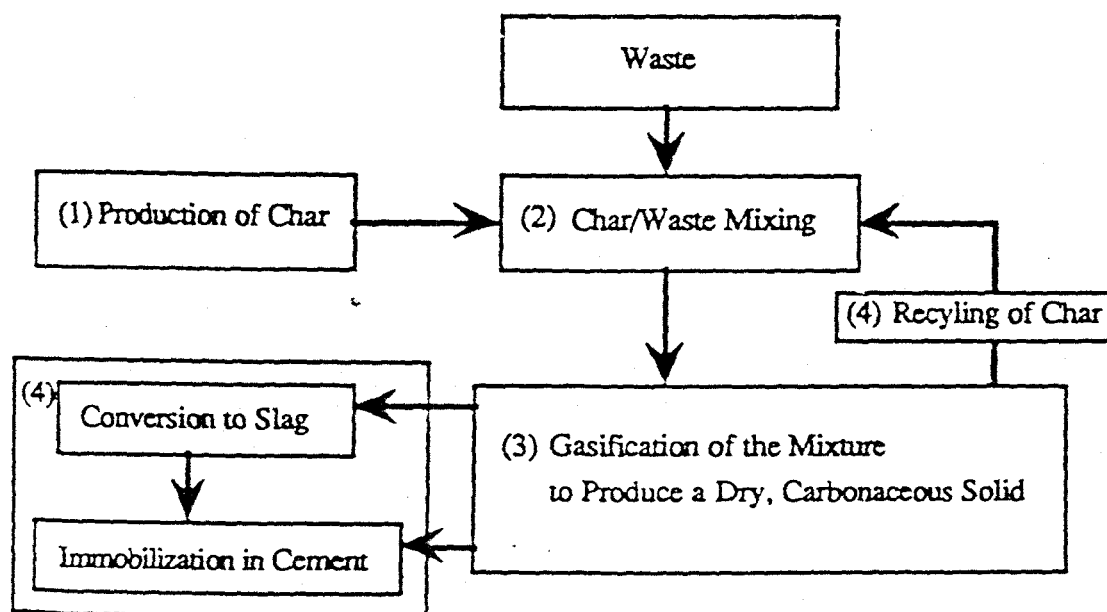

Figure 1-1. Flow diagram of the ChemChar Process for hazardous waste treatment.

(1) **Production of activated char.** Activated char is produced from Rosebud subbituminous coal from Hanna, Wyoming. The reactor consists of a 1 inch inner diameter, 12 inch long Vycor® tube packed with 20-80 mesh (average size ~ 1 mm) coal (Figure 1-2). The coal is held in the tube with a plug of silica wool in the bottom. Dry oxygen gas flows downward through the column. A flame front is initiated at the bottom of the column of coal by external heating with a torch. The ~1200 °C glowing red flame front moves evenly upward in the direction counter to the flow of gas, hence the name "reverse-burn," leaving a column of char as a portion of the coal is gasified. The product gas is a multi-component combustible mixture containing appreciable amounts of carbon monoxide and hydrogen. The reverse-burn can be repeated twice more to produce triple-reverse-burn char (TRB Char).

(2) **Contacting the activated char with waste.** A multitude of different waste types are treatable with the ChemChar Process. Liquid wastes can be sorbed directly onto the char surface. Aqueous wastes can be filtered through a bed of char to remove hazardous materials. The purified water can be discharged and the char dried and gasified. Waste sludges can be mixed directly with char by adding solvents or enough char to prevent agglomeration. The char particles act to dry these types of wastes through capillary action of the micropores in the char. Solid wastes can be macerated and mixed directly with char before being fed into the reactor.

(3) **Gasification of the char/waste mixture.** The same basic apparatus is used for the reverse-burn gasification of wastes. The waste material must be intimately contacted with activated char particles for optimal gasification. Energy for the process is generated by exothermic reactions of oxygen with the reactor charge; coal, char, or waste materials sorbed on the carbon. The following reactions occur:
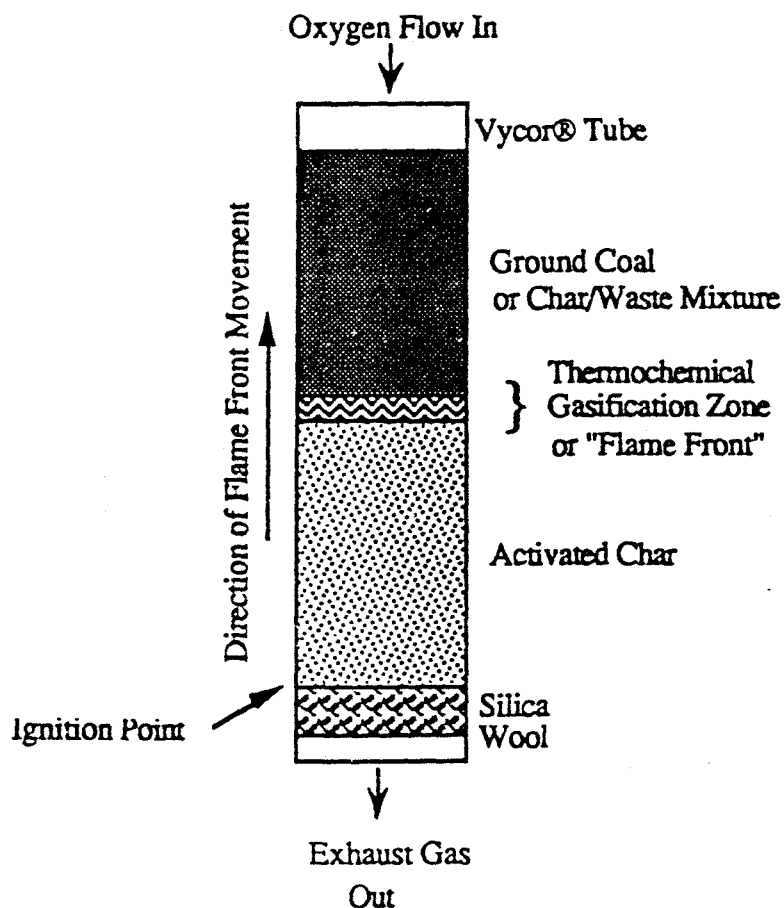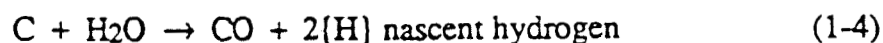
$$C + O_2 \rightarrow CO_2 + heat \qquad\qquad (1\text{-}1)$$

$$2C + O_2 \rightarrow 2CO + heat \qquad\qquad (1\text{-}2)$$

$$4H(\text{from waste}) + O_2 \rightarrow 2H_2O + heat \qquad\qquad (1\text{-}3)$$

Oxygen Flow In

Direction of Flame Front Movement

Vycor® Tube

Ground Coal
or Char/Waste Mixture

} Thermochemical
Gasification Zone
or "Flame Front"

Activated Char

Ignition Point

Silica
Wool

Exhaust Gas
Out

Figure 1-2. Diagram of the ChemChar Reverse-Burn Gasification reactor for the production of activated char and the destruction of hazardous waste.

These reactions occur at the front of the gasification zone where there the atmosphere is rich in oxygen. Heat generated by these reactions pyrolyzes wastes sorbed to or mixed

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with the carbon and provides energy for the following endothermic reactions to occur in the downstream end of the gasification zone:

$$C + H_2O \rightarrow CO + 2\{H\} \text{ nascent hydrogen} \qquad (1\text{-}4)$$

$$2\{H\} \rightarrow H_2 \qquad (1\text{-}5)$$

$$CO_2 + C \rightarrow 2CO \qquad (1\text{-}6)$$

The products of these reactions are reducing gases which create a strongly reducing atmosphere behind the flame front.

The oxygen flow to the reactor is halted when the flame front reaches the top of the tube. Ash can be produced in the same apparatus by first performing a reverse-burn on the reactor charge and then by continuing the flow of oxygen after it has reached the top of the column. The flame front reverses direction and continues to burn until all of the carbon is consumed leaving an ash residue. This is called the "forward-burn" mode.

(4) Recycling of the char or fixation of the non-recyclable char or ash. Because metals are retained in the char, the process can be effective in treating mixed wastes. Wastes containing mixtures of organics and heavy metals can be treated as well with retention of the heavy metals, except for mercury. The product of the gasification is a dry granular reactivated char which is easy to manipulate and amenable to fixation in cement. If the ash content and the amount of fines in the char remains low, the char may be recycled through numerous waste mixing and reverse-burn cycles.

The gasification process occurs in a non-turbulent bed of carbon, therefore no fly ash is produced while operating in the reverse-burn mode. Potential solid pollutants are retained in the char and the char can be treated to neutralize acid gases produced. Because the off-gases are hydrogen and carbon monoxide, they can be used as fuel.

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The ChemChar Reverse-Burn Gasification Process for the treatment of hazardous waste is still in its infancy yet it shows great promise as an inexpensive and effective method for the reduction and immobilization of a wide variety of hazardous waste materials.

In the late 1970's, an apparatus (Figure 1-3) for the laboratory simulation of underground coal gasification was developed by Stanley. E. Manahan and Darryl Bornhop at the University of Missouri-Columbia for use in studies of groundwater pollution resulting from underground coal gasification.[11] Rosebud subbituminous coal from Hanna, Wyoming was selected for the study. The reactor consisted of a 15 mm inner diameter, 30 cm long Vycor® tube packed with 20-60 mesh (0.18-0.8 mm) coal. The coal was held in the tube with a plug of glass wool in the bottom. A stream of oxygen gas, saturated with water vapor by bubbling it through water heated to 90 °C, flowed downward through the column. A flame front was initiated at the bottom of the column of coal by external heating with a torch. The flame front moved evenly upward in the direction counter to the flow of gas leaving a column of char as a portion of the coal was gasified. The oxygen flow to the reactor was halted when the flame front reached the top of the coal in the tube. The product gas was combustible. Ash was produced in the same apparatus by first performing a reverse-burn on the coal in the reactor and then continuing the flow of oxygen thus allowing the flame front to reverse direction after it had reached the top of the coal column. In the forward-burn mode, the char was consumed leaving an ash.

The coal and coal-derived products, such as char and ash, produced in the process were evaluated as possible sorbents for organic and inorganic pollutants resulting from underground coal gasification. The order of increasing effectiveness of sorption of these solids was determined to be char < coal < ash. The ineffectiveness of the char was thought to be a result of tar residue from the single reverse-burn gasification of coal which had
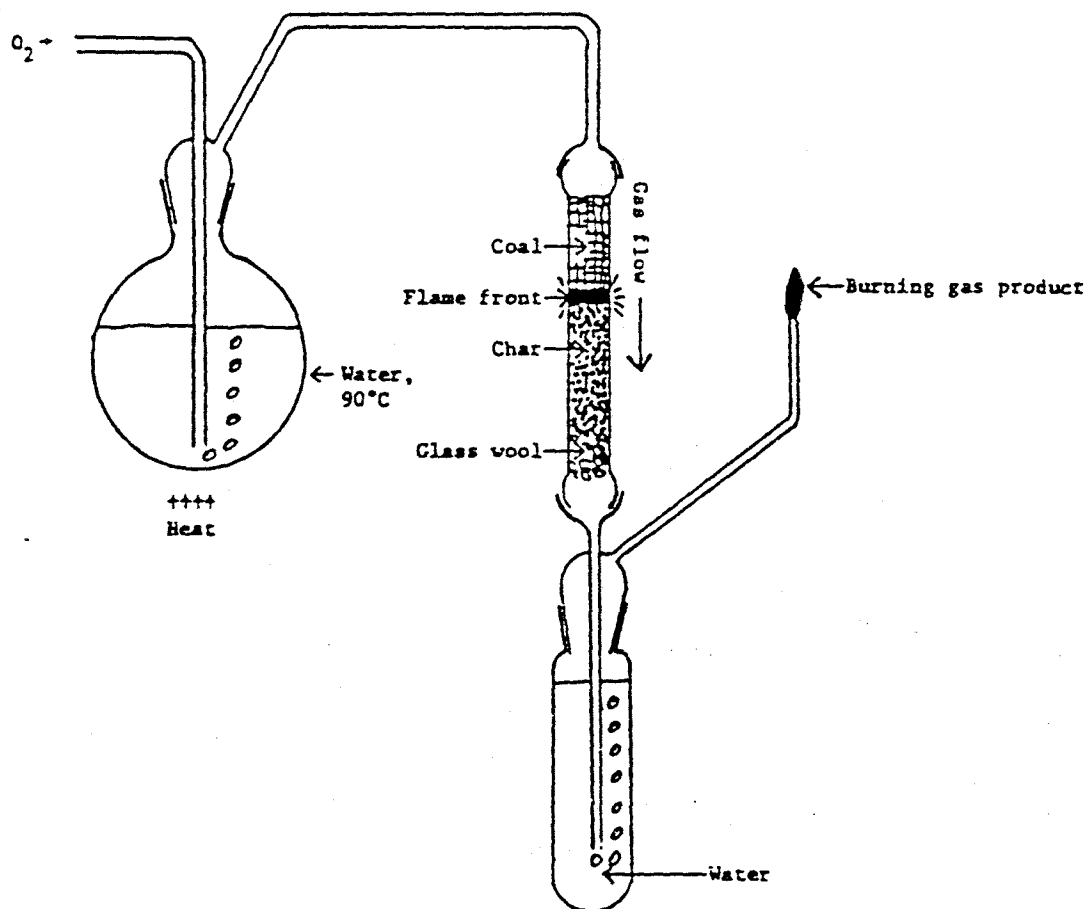
coated the surface and the pores.

Figure 1-3. Apparatus for simulated underground gasification of coal used for preparation of char and collection of contaminated by-products.[11]

In the early 1980's, while performing graduate work under the advisement of S. E. Manahan, Robert Gale reported an increase in the sorptive characteristics of reverse-burned coal char by subjecting it to multiple reverse-burn gasifications to produce a multiply revese-burned char (MRBC).[12] Multiple reverse-burn treatment of the coal char was done to remove the tar deposited in the first reverse-burn gasification, create active oxidized sites on the char surface, and increase the surface area of the char by burn-off to develop an increased microporous structure.

To produce MRBC, a reverse-burn gasification of coal was performed as usual and the flame front was extinguished by termination of the support gas flow after the flame front had reached the top of the char column. After the flame zone temperature had decreased to a point where re-ignition would not occur, the flame front was re-ignited at the downstream end of the column. This cycle was repeated a third time to produce char which had been gasified three times. Organic vapors decreased with successive reverse-burns and the flame front moved faster each time indicating that less of the char surface was being oxidized. The product was a dry, granular, highly macroporous carbon with increased surface area (> 200 m^2/g). Studies of the sorption of metals from water confirmed the enhanced sorptive characteristics of MRBC. Removal of 100 % (within the limit of detection by atomic absorption) of Cu, Ni, Cd, Zn, Cr(III), and Cr (VI) from aqueous solution within 10 minutes was reported.

In 1985, while consulting on a project concerning the disposal of arsenic sulfide sludge, Manahan conceived the idea of adding coal char to sludge to facilitate drying by capillary action of the char and produce a solid more amenable to fixation in cement.[13] The mixture was also reverse-burned to destroy the organics. This type of waste product soon became known as "Stan-crete."

The use of coal char for waste treatment caught the interest of David Larsen at the University of Missouri-St. Louis and the idea for the implementation of char as a substrate and fuel for the reverse-burn gasification of hazardous waste was developed. Operational parameters for the production of triple-reverse-burned char (TRB Char) were determined and the two formed ChemChar Research, Inc. in 1989 and obtained a patent for the process in December, 1990.[14] The reverse-burn gasification of waste became known as the ChemChar Process for thermal treatment of hazardous waste.

Although the basic apparatus for reverse-burn gasification has remained basically the same since its inception, studies of the application of reverse-burn gasification technology

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to waste treatment have shown that it can be used to treat a wide variety of different waste forms.

Some preliminary work was done by J. Chris Cady on the treatment of hazardous wastes by reverse-burn gasification.[15] Triple-reverse-burned char was used to treat a sludge containing polychlorinated biphenyls (PCBs). The destruction efficiency for the PCB, Aroclor, was determined to be 99.76 %. Soils contaminated with pentachlorophenol (PCP) and hexachlorobenzene (HCB) were mixed with TRB Char and gasified. Destruction efficiencies of 99.9 % were reported. Chromatographic properties of TRB Char were investigated with the achievement of separation of planar and non-planar PCBs. Regeneration of commercially available granular activated carbon (GAC) was reported by reverse-burn gasification, however, true regeneration was not actually performed because the carbons were not spent prior to reverse-burning.

This dissertation presents the application of the ChemChar Process to the treatment of "mixed waste" which is a combination of radioactive and organic waste. Organic ion exchange resins containing metals, to simulate waste resins used to remove ions from cooling water in nuclear reactors, were gasified to destroy the organic content of the resin while retaining the metals. The char and ash products of the resin destruction were fixed in Portland cement and subjected to leach and strength testing. Tracking of metals by atomic absorption and tracer studies showed the ability of the char and ash to retain metals throughout the process.

The application of petroleum coke as an alternative form of activated carbon to use as a substrate for the reverse-burn treatment of wastes was also explored. Reagents were added to the carbon matrix to act as catalysts in waste gasification and improve the physical quality of the product. The addition of iron appeared to have catalytic effects in the destruction of hexachlorobenzene.

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The fate of mercury in the ChemChar Process was investigated by gasifying mercury-loaded char. Mercury emission from the reactor was substantial, however, a TRB Char trap downstream proved to be an excellent adsorbent for escaping mercury vapor.

Spent granular activated carbons were regenerated by reverse-burn gasification. The sorptive capacities and surface areas of selected regenerated carbons were determined to be comparable to the original carbon. Activated carbons used to treat wastewater may be regenerated by this method.

The development of the process is continuing with investigations by Laura Kinner who is testing for PCDD, PCDF, and PCB formation on the char and in effluent gases during the gasification of chlorinated aromatics contained in mixed wastes.

CHAPTER 2

TREATMENT OF WASTE RADIOACTIVE ION EXCHANGE RESINS
BY REVERSE-BURN GASIFICATION

INTRODUCTION

The Use of Ion Exchange Resins in Radioactive Wastewater Treatment

Ion exchange is used for treatment of low ionic strength liquid radioactive waste. In those nuclear reactors where water is used as the primary coolant, ion exchange resins are a necessity for minimizing corrosion and protecting all heat transfer surfaces from scaling. Ion exchange resins are insoluble, high molecular weight styrene-divinylbenzene copolymers with active functional groups attached. The functional groups can reversibly exchange their mobile ions with those of like charge from the surrounding solution. Strong-acid cation exchange resins and strong-base anion exchange resins are typically used in nuclear power plants. Strong-acid cation exchange resins contain H^+ as the mobile exchange ion and strong-base anion exchange resins are in the OH^- form.

The water quality used for cooling in nuclear power plants must be very high to minimize corrosion problems and the formation of neutron activation products. As an additional aid for the reduction of corrosion, these resins provide a method for controlling pH of the coolant water at a value least conducive to attack of the metal surfaces by this water. In order to minimize chloride stress corrosion, chloride has been reduced in these resins.[16] Ion exchange resins of higher purity than those normally employed in water conditioning applications have been found more desireable for the treatment of water in nuclear power plants.

Mixed-bed systems are the most frequently employed in water and waste treatment. This usually consists of a 2-8 foot deep fixed bed of a mixture of anion and cation

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exchange resins. A disadvantage of strong-acid or strong-base ion exchange resins is their low regeneration efficiencies. Regeneration of the spent resin mixtures can be achieved if the resins are separated by flotation, rinsed to regenerate, and then re-mixed. However, spent resin beds are usually discarded rather than regenerated due to the time and processing required for regeneration and the low efficiency achieved.

The disposal of radioactive waste is strictly regulated.[17] Waste resins are commonly mixed with cement to prevent leaching after disposal. Two fundamental problems that are inherent with resin/cement mixtures are that resins are basically incompatible with cement and resins and polymers are subject to radiolytic decomposition and degradation.[18] The organic content of the resin presents a problem in the fixation of the waste. As the concrete cures, shrinkage of the resin as it dries can create large pores which weaken the structural integrity of the final concrete product. The resin may also decompose to yield gases and organic compounds which degrade and weaken the concrete and contribute to leaching. The organic resin components can also undergo radiolytic decomposition. These factors lead to cracking and deformation of the resin/cement mixture. The leach resistance of the cemented ash is poor. Presently, the resin to cement mass ratio which is needed to form a suitable solid product is 1 to 50.[19,20] Cementized dried resins must pass a 50 psi compressive strength test after 90 days immersion in water.

Incineration of waste resins is possible in some cases; however, many metals are volatile at the temperatures needed to destroy the organic matrix.[21] Incineration produces fly-ash to which vaporized metals can cling. During the incineration process these metals will enter the atmosphere if special stack filtering equipment is not employed. This is especially dangerous when the resin has been utilized in the removal of radioactive ions. Cesium-130 and strontium-90 are examples of metals which are commonly found in radioactive waste which can be volatilized.

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Brief Description of the Process to Treat the Spent Resins

The reverse-burn process acts in an effective and economical manner to dewater resins and to destroy the organic resin components in the presence of the inorganic components. The innovative aspect of the process is that the spent resin is dispersed with an activated char, which is then subjected to a unique reverse burn gasification. Char gasification produces a high temperature, chemically reducing environment that converts the organic resin to a char material. Unlike conventional incineration processes, the reverse-burn process does not depend upon very high temperatures and turbulence to destroy organic wastes. This places relatively less demand upon the materials used to construct the treatment reactor and provides a greater margin of safety. Under the gasification conditions used in the reverse-burn treatment process, the organic components are destroyed and water is evaporated, while the inorganic components, including radionuclides bound to the resin, are retained on the carbon matrix. The carbon product can be set in cement, converted to a small-volume mineral slag, or glassified. Reverse burn gasification accomplishes a substantial volume reduction of at least two-fold. An even greater volume reduction (>20-fold) can be achieved with a subsequent complete forward burn gasification of the char/inorganic mass. This leads to containment of the inorganics in a leach-resistant slag or glass that has a much smaller volume than the original resin. Heat for the process is obtained directly from the char gasification and no external heat source is required.

The reverse-burn process destroys the organics and leaves only inorganics, including the radionuclides, char, and mineral slag; these components are all very compatable with cement.

The process involves four key steps:

(1) Production of an activated char from subbituminous coal by a multiple reverse-burn gasification procedure.

(2) Contacting the char and resin to form an intimate mixture.

(3) Reverse burn gasification of the char/resin mixture to destroy the organic components while fixing the inorganic components.

(4) Setting the char/inorganic mass in cement or reduction of the char/inorganic mass to a small volume of leach-resistant silicaceous slag by complete forward burn gasification of the remaining char.

The gasified char/inorganic product from step 3 can be recycled through steps 2 and 3.

The process is illustrated schematically in Figure 2-1.
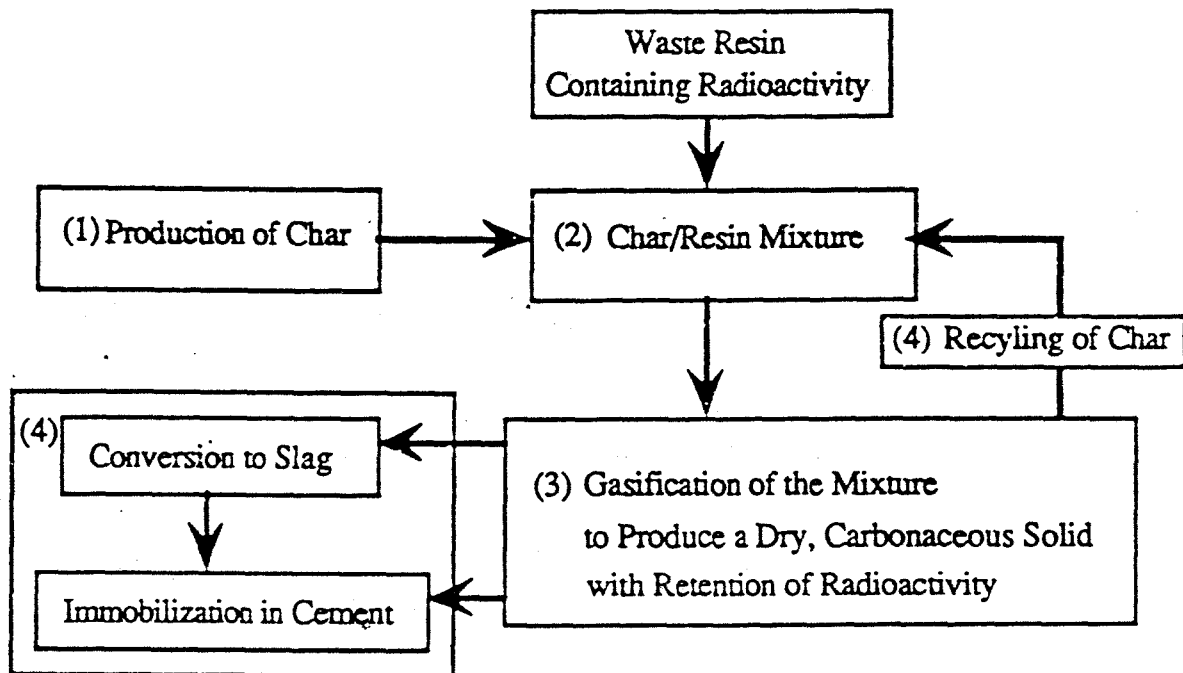
Figure 2-1. Schematic of process steps in treatment of waste organic ion exchange resins.

Destruction of the Organic Components and Dewatering by Reverse-Burn Gasification

Many of the problems associated with waste ion exchange resins are a result of their high moisture content. They can swell up to 50 % when wet making them quite bulky and

a significant amount of moisture can remain even after air drying. The residual water can facilitate leaching of the sorbed waste ions thus reversing the intended purpose of the resin in the waste treatment process.

Activated carbon has been widely used for organic and inorganic waste treatment.[22,23,24,25,26] Activated coal char made by the reverse-burn process has unique properties that are crucial to its use for resin treatment. The mechanically stable nature of the char and its high volume of relatively large pores provides an ideal physical matrix for mixing, drying and retention of organic materials. The char also provides a surface on which thermochemical reactions can occur to destroy the organic component of the resin. Gasification of the char provides both heat and a reducing atmosphere for chemical reactions to destroy organics at elevated temperature. Most importantly, no fly ash is produced in the gasification process.

Following its preparation and drying, the char/resin mixture is subjected to reverse-burn gasification to destroy the organic components as illustrated in Figure 2-1. The resin is converted partly to solid carbon, as well as to gaseous products—carbon monoxide, carbon dioxide. Hydrogen sulfide, nitrogen, and ammonia can be produced depending upon the type of active groups present on the resin. About 10 % of the char is consumed in the reverse-burn gasification process.

To further reduce the volume of spent organic resins, the reverse-burned char/resin mixtures may be recycled by mixing with more spent resin for another reverse-burn gasification. This procedure may be repeated several times before fixation and/or complete oxidation.

Retention of Metals in the Process

Common contaminants of reactor wastewater include ^{90}Sr and [137]Cs.[27] Due to its chemical similarity to Ca, ^{90}Sr is potentially hazardous because it can be introduced into the food chain.

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Metal retention in waste treatment can be measured using a radionuclide tracer, technetium-99m. In addition to being a significant contaminant nuclear fission by-product, this radionuclide is a standard one[28] used for a wide range of radiotracer and imaging studies because of its optimum half-life and radiation charcteristics. Technetium-99m is generated as a decay product of ^{99}Mo and can be eluted from the generator as the pertechnetate ion, $^{99m}TcO_4^-$.[29] The activity of ^{99m}Tc can be counted with a well-type NaI(T1) solid scintillation detector to measure the 140.5-keV γ emission.[30]

Fixation by Solidification of the Inorganic Components

After the organic components have been destroyed, fixation of the inorganic components can be accomplished in three possible ways. The char/resin reverse-burn residue can be used as an aggregate and set in cement. The mixture can be reduced to a slag by a complete forward-burn of all the remaining char, a mode of gasification in which the flame front moves in the same direction as the oxidant flow as described in Chapter 1. The carbon in the char is completely oxidized in a forward-burn. The mixture can be vitrified by adding silica to the char product prior to forward-burn gasification.[20]

This chapter describes experiments performed to determine the feasibility of using TRB Char and reverse-burn gasification for the destruction and fixation of waste ion exchange resins. Parameters investigated were; the determination of requirements for contacting char and resin, the retention of metals by the process, the feasibility of recycling the gasified residue, and the residue to cement mass ratio necessary to form a stable final disposal product.

EXPERIMENTAL

Reagents

Triple-reverse-burned coal char (TRB Char) was produced by reverse-burning ground

Wyoming subbituminous coal three times as described in the previous chapter and sieved to a mesh size of 20-60 (~1 mm diameter). Amberlite IR-124 cation exchange resin manufactured by Rohm and Haas is commonly used to recover metals from rinse water and cooling water. It is a styrene-divinylbenzene type (12 % DVB) in the sodium form consisting of gold-colored beads of mesh size 20-50 and an effective size of about 0.5 mm. The approximate moisture content is 39 % and it has an ion exchange capacity of 5.0 meq/g. The active sites are sulfite groups, $-SO_3^-$. Amberlite IRN-77 is a nuclear grade cation exchange resin. It is a strongly acidic cation exchange resin with a minimum of 98 % of its exchange sites in the hydrogen form. The particle size ranges from 16-50 mesh with an effective size of 0.45-0.60 mm and a capacity of 38.2 kg $CaCO_3/ft.^3$. The maximum moisture content is 55 %. Amberlite IRN-78 is a nuclear grade anion exchange resin. It is a strongly basic anion exchange resin containing a minimum of 85 % of the exchange sites in the OH form and a capacity of 26.2 kg $CaCO_3/ft.^3$. The particle size ranges from 16-50 mesh with an effective size of 0.38-0.45 mm. The maximum moisture content is 60 %. Samples of Amberlite IRN-77 and IRN-78 were obtained from Missouri University Research Reactor (MURR) and have been used there to remove radioactive ions from cooling water.

All metal solutions added to the resins were made from analytical grade metal salts. Standards used in the analysis of samples by flame atomic absorption spectroscopy (AAS), inductively-coupled plasma-atomic emission spectroscopy (ICP-AES), and for the leaching study were prepared by dilution of commercially available atomic absorption standards. These standards typically contain 1000 μg/mL (ppm) metal in 1 % HNO_3 or HCl.

Technetium-99m was produced from the decay of $^{99}MoO_4^{2-}$ on an activated alumina column. ^{99m}Tc is eluted from the column with normal saline solution as $^{99m}TcO_4^-$.

Standard commercial grade Portland cement was used for fixation of the resin and reduced resin/char aggregates.

Apparatus

The same reactor design used to produce TRB Char, as described in Chapter 1, was also utilized for the gasification and conversion to slag of the resin/TRB Char mixtures (Figure 2-2). A 1 inch diameter Vycor® tube was fitted with two steel endcaps attached with J-B Weld® epoxy. The gasifying mixture was held in place by a plug of silica wool. A series of two gas washing traps were installed to recover metal vapor from the exhaust stream. Tygon® tubing connected the reactor exhaust port to the two traps. The reverse burn was ignited by heating with a propane torch at the bottom of the column. After a reverse-burn was completed, the oxygen flow was stopped if the desired product was the char with charred resin. However, if the desired product was an ash or slag, the oxygen flow was reduced but maintained after the flame front reached the top of the reactor tube. This allowed for slow, but complete oxidation of the reactor charge.

Contacting TRB Char with Resin and Retention of Nickel by Ash

TRB Char must be evenly dispersed with the waste resin before effective gasification can occur. A method was developed for contacting TRB Char with resin. Prior to mixing, the granular char was reduced to small particles of 20-80 mesh. The dry Amberlite IR-124 cation exchange resin did not disperse well when mixed with char, therefore, the resin was slurried in deionized water. About a 50 % swelling in volume was observed after several hours and the slurry contained approximately 50 % water by weight. This resin slurry was easy to transfer and mixed readily with the char by simple stirring. It was determined that the optimum gasification of resin requires that the slurry/char mixture must be air-dried to remove the excess water. The char particles in the slurry facilitated the drying by capillary action. Some residual water within the resin particles was not removed by air drying. The TRB Char particles adhered to the resin particles upon air-drying if they were smaller in size than the resin particles. The amount of TRB Char mixed with 20.0 g samples of resin
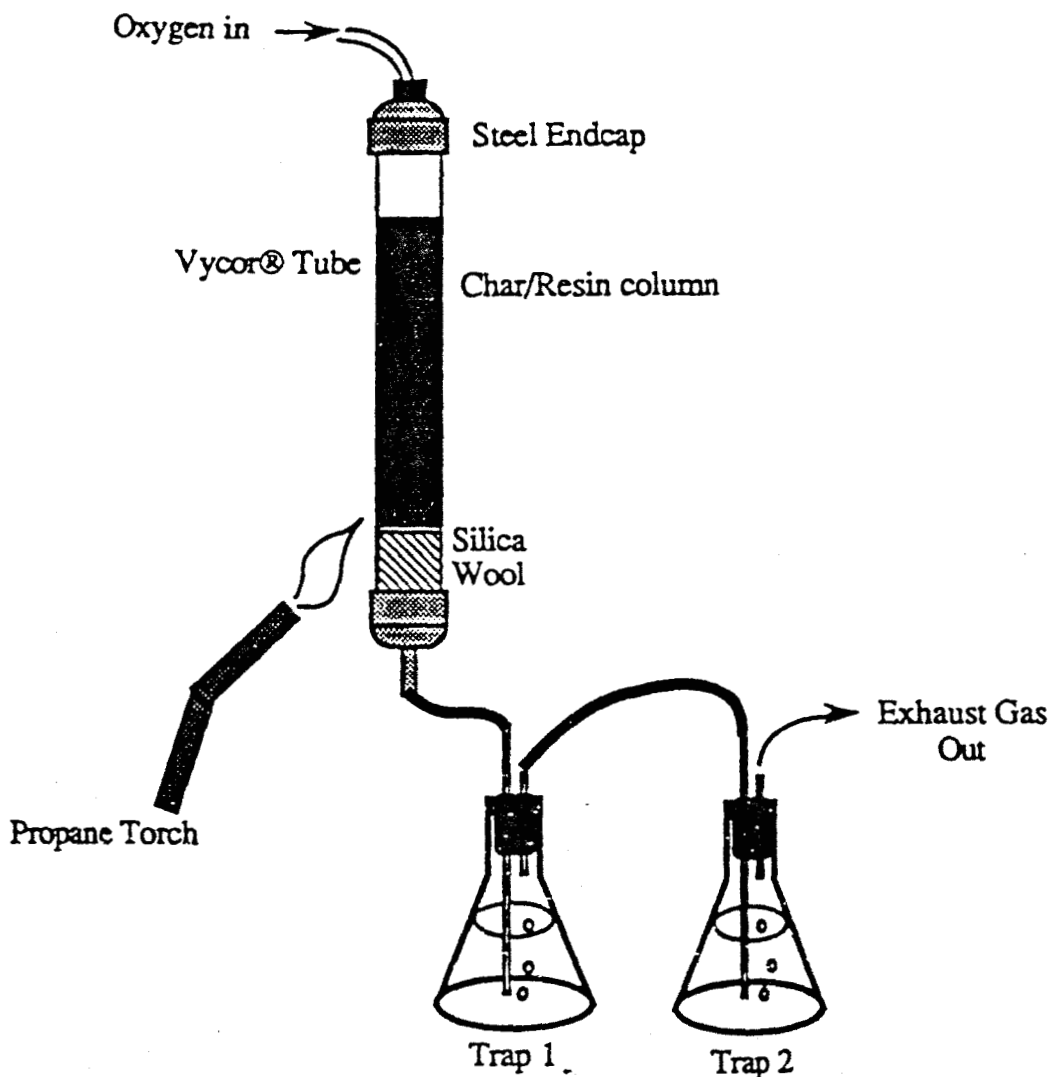
Figure 2-2. Reactor design for the gasification of ion exchange resins.

slurry was varied and the behavior of the mixture during gasification was evaluated to determine the optimum ratio of char to resin slurry. Table 2-1 lists the amounts of TRB Char added to each sample. As it gasified, each sample was observed to determine if the flame front was relatively even across the reactor (no channeling) in the reverse-burn mode and if the resin was completely converted to ash in the subsequent forward-burn mode.

TABLE 2-1

TRB Char to Resin Slurry Ratio in Determination of Gasification Requirements

Sample number	Mass of Char	Mass of Resin Slurry	Mass Ratio Char/Resin Slurry
1	0.0 g	20.0 g	0 %
2	2.0 g	20.0 g	10 %
3	4.0 g	20.0 g	20 %
4	6.0 g	20.0 g	30 %
5	8.0 g	20.0 g	40 %

Each 20.0 g of slurry was spiked with 1.0 mL of a 1000 ppm Ni standard solution (1 % in HNO_3) to give an overall loading of 1 mg Ni. The resin was stirred manually to allow the Ni to exchange evenly onto the resin. The resins were then mixed with the various amounts of char, covered loosely, and air-dried before gasification.

An oxygen flow of 0.824 L/min was used for the reverse-burn after which the burn tube was rotated to a horizontal position and a flow rate of 0.3674 L/min was set for the ashing of each sample. The residue in the burn tube was transferred quantitatively out into a sample bottle and the tube was rinsed with concentrated HNO_3 then deionized (D.I.) water. The combined rinses and ash were subjected to a wet acid digestion from 30 mL concentrated HNO_3 to ~10 mL. After filtering and diluting to 250 ml in D.I. water, the solutions were analyzed by atomic absorption. Ni concentration was also determined in a blank sample of 5.0 g TRB Char that was forward-burned to ash. No traps were used in this experiment.

Retention of Cesium and Strontium by the Char/Resin Residue During Reverse-Burn Gasification

A study was done to measure the ability of the resin/char column to retain cesium and strontium during gasification. A 2 mL spike from a solution containing 5000 ppm of nonradioactive isotopes of Sr and Cs was added to two identical 20.0 g Amberlite IR-124 cation exchange resin slurry (in D. I. water) samples. This gave a total amount of 10 mg of each metal added to each resin sample. Each spiked slurry was mixed with 6.0 g of 20-60 mesh ground TRB Char. The samples were allowed to air dry overnight and subsequently reverse-burn gasified. Gas emerging from the reactor was bubbled through two sequential 200 mL traps containing 5 % HNO_3 solution to trap any volatile metal vapors which might evolve during the reverse-burn. Following gasification, the reactor resin/char product was extracted by equilibrating three times with 5 % HNO_3 and washing to a total volume of 500 mL. The silica wool plug was included with the char during the extraction. The solution in each trap was analyzed by flame AAS for Cs and Sr. Lanthanum was added as a matrix modifier for the analysis of Sr to prevent interference from Al.

Retention of Radioactive Technetium-99m

In order to refine the measurement of metal retention by the resin/char column, the study was performed using technetium-99m as a radiotracer. A sample containing ^{99m}Tc as TcO_4^- was loaded on an anion exchange resin (Amberlite IRN-78), and the resin slurry was mixed with char in a 10:3 ratio. The resin/char mixture was air dried and charged into the reactor. The reactor was configured so that oxidant flow was upward to avoid the potential problem of water elution described above. A TRB Char filter was added to the column after the char/resin mixture as a precautionary measure for adsorption of volatilized components. The reactor configuration is shown in Figure 2-3. The resin/char mixture was subjected to reverse burn gasification and the activities of 1 cm^3 volumes of resin/char product, glass wool, and filter char were measured. Evolution of ammonia was observed

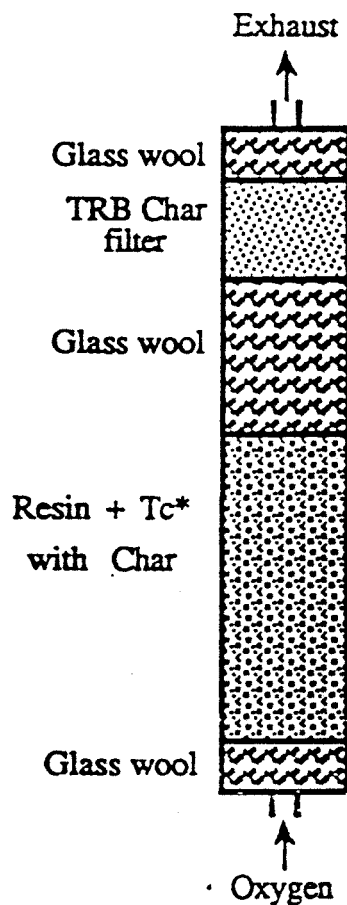during the gasification resulting from amine groups on the resin.

Exhaust

Glass wool

TRB Char
filter

Glass wool

Resin + Tc*
with Char

Glass wool

· Oxygen

Figure 2-3. Reactor configuration employed in the technetium-99m retention experiment.

Destruction of the Organic Matrix of the Resin and Removal of Water by Reverse-Burn Gasification

Duplicate samples of resin/char mixtures in a ratio of 10 parts slurry to 3 parts TRB Char by mass were prepared and allowed to air dry. Each sample was treated to five reverse-burn cycles. After each cycle, the mass of the sample was recorded. The mass loss resulting from each reverse-burn was compared to the mass loss for coal char alone

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throughout several reverse-burn cycles. The initially higher rate of burn-off for the resin/char mixtures indicated the degree of destruction of the resin in the mixture.

Surface Analysis of Reverse-Burn Gasification Product

Scanning electron micrographs (SEMs) were obtained of a reverse-burned Amberlite IR-124 resin/char sample. The sample was coated with a thin layer of vapor-deposited gold to prevent sputtering of the sample by the electron beam. Energy dispersive x-ray analysis (EDAX) was performed on the surface to determine the elemental composition of deposits seen in the micrograph.

Recycling of TRB Char/Resin Residue

To further reduce the volume of spent organic resins, the reverse-burned char/resin mixtures were mixed with more spent resin for another reverse-burn gasification. A mixed-bed ion exchange resin was prepared by mixing 10.0 g of Amberlite IRN-77 cation and 10.0 g Amberlite IRN-78 anion exchange resin slurries. For the recycling experiment, duplicate samples were prepared by adding 2.0 mL of a standard solution containing 5 mg each of Sr, Cs. Ni, and Cr as chromate ion. Each resin was then mixed with 6 g of TRB Char and allowed to air dry. The samples were reverse-burned twice in the reactor shown in Figure 2-2, then mixed with another aliquot of metal-spiked resin, air-dried, and reverse-burned twice again. This cycle was repeated once more so that a total of 60 g of wet resin had been treated and 15 mg of each metal had been added. A one-gram plug of TRB Char was placed below the sample in the reactor to aid in the establishment of an even flame front.

The exhaust gas was bubbled through 200 mL of 3 % HNO_3. Fresh acid solution was used for each of the three cycles. These solutions were diluted to 250 mL and analyzed by flame AAS for each metal that was added.

In the ashing experiment, two identical samples were prepared by adding 4 mL of the same standard solution (10 mg of each metal total) to 20 g of mixed resin. This was mixed

with 6 g of TRB Char and air dried. Each sample was oxidized completely to ash. A series of two traps were used in sequence for each sample. Each trap contained 200 mL of 3 % HNO_3. These solution were also diluted to 250 mL and analyzed by flame AAS. Lanthanum was added to each sample to prevent interference from Al in the analysis of Sr.

Fixation of Gasification Products in Cement

The reverse-burn gasification product of spent char/resin mixtures was a hard, porous, granular char. It could be poured easily from the reactor and readily mixed with Portland cement to form a stable composite. The product obtained by reverse-burning then forward-burning the char/resin mixture was an ash residue. The volume reduction of spent resin was maximized by performing a forward burn; however, the ash was more difficult to handle and the forward burn mode produced fly ash.

Sample concrete plugs were prepared by mixing air-dried resin and resin gasification products with Portland cement. The resin gasification products were produced by reverse-burn gasification of 10:3 ratio mixtures of resin slurry to TRB Char. The products were then mixed in varying ratios with cement as aggregate to produce a form of concrete. Preliminary research had shown that a superior product was obtained by wetting the cement before mixing it with the resin/char aggregate. Mixing the dry char and cement together before adding water gave a poor product. Mixing the cement with water first activates the cement before mixing with char. The aggregate/cement mixtures were poured into paper forms to produce cylindrical plugs 2 inches long and 1 inch in diameter. The concrete material was allowed to cure for one week with regular applications of water to keep it moist, after which time the forms were removed and the plugs allowed to dry in contact with the atmosphere for two weeks. The compressive strength of each sample was determined by compression in a hydraulic pressure system which measured the amount of pressure in pounds that could be applied to the sample before it developed a stress fracture.

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Leachability of the Final Cement Product

The leachability of the final cement product was tested according to the Environmental Protection Agency (EPA) Standard Method 1310 for five metals. Amberlite IRN-77 was slurried in D. I. water for 30 minutes and weighed out into 20 g aliquots. Samples 1 and 2 were spiked with 15 mL of a standard solution containing 200 ppm each of iron, zinc, cobalt, chromium, and manganese, to give a loading of 3 mg of each metal per sample. Samples 3, 4, and 5 were spiked with 10 mL of the standard solution to give a loading of 2 mg each metal. The resins were equilibrated for 30 minutes and mixed with 6 g of coal char. The samples were allowed to air dry overnight.

The next day, each mixture was reverse-burned one time, removed from the column, allowed to cool, and weighed. A mass of Portland cement equal to the mass of the resin/char residue was added. Water was added to make a slurry or paste. Table 2-2 lists the composition of each sample. Styrofoam cups served as molds for the concrete.

TABLE 2-2

Composition of Cement/Resin/Char Aggregate Samples

Sample	mg each metal	Mass Ratio Resin slurry:Char	Mass after 1RB	Mass Cement	Volume water
1	3	20:6	14 g	14 g	25 mL
2.	3	20:6	16 g	16 g	30 mL
3	2	20:6	13 g	13 g	25 mL
4	2	20:6	12 g	12 g	31 mL
5	2	20:6	10 g	10 g	27 mL

After curing for 7 days, the concrete plugs were broken up with a hammer into 1 cm pieces. The leaching procedure was then carried out as indicated. A blank sample was included. Several modifications were made in the procedure. Sample sizes were reduced as the equipment available could not accomodate the larger sizes specified. The shaker used was a reciprocating (back-and-forth) shaker.

A mass of 30 g of concrete sample was placed in a 500 mL screw cap bottle with 400 mL of D. I. water. As required by the standard procedure, the pH of the leachate was kept at 5 ± 0.2. Due to the strongly alkaline nature of cement, 0.5 M acetic acid had to be added to the samples periodically to readjust pH. The maximum allowable amount of acid pH adjuster was not exceeded.

After 24 hours leach time, the samples were filtered through a medium porosity filter paper, and then through a 0.5 μm Millipore filter under vacuum. The samples were brought to the required final volume of 600 mL. The samples were prepared for analysis by ICP-AES by combining 98 mL with 2 ml of concentrated distilled nitric acid.

RESULTS AND DISCUSSION

Contacting TRB Char with Resin and Retention of Nickel by Ash

An even flame front was observed when sample 1 was reverse-burned. This sample, which contained only resin with no char added, gasified very rapidly. The effluent gas was strongly acidic and H_2S smell emerged from the reactor with a fine yellow aerosol of elemental sulfur. Forward-burning left only a small amount of tar residue. The production of sulfur gases was expected as the ion exchange groups on the resin were sulfite groups.

Samples containing TRB Char produced basic ash after forward-burning and all reverse-burned evenly. It was found that 20 g of resin slurry could be satisfactorily gasified with as little as 6 g of char. A well behaved flame front was observed and a combustible gas was produced.

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The recovery of nickel in the samples (Table 2-3) showed that a 30 % mass ratio of TRB Char to resin slurry gave complete recovery of nickel from the ash with a minimum of TRB Char added. No detectible Ni was found in the TRB Char blank. The detection limit for nickel was determined to be 0.1 ppm or a total of 0.025 mg (2.5 %).

TABLE 2-3

Percent Recovery of Nickel for Various Char/Resin Slurry Mass Ratios

Sample number	Mass Ratio Char/Resin Slurry	Recovery of Nickel
1	0 %	83.75 %
2	10 %	88.25 %
3	20 %	88.75 %
4	30 %	101.25 %
5	40 %	106.25 %

Retention of Cesium and Strontium by the Char/Resin Residue During Reverse-Burn Gasification

The results for Sr and Cs shown in Table 2-4 show that there is very minimal, if any, loss of metal vapor during the reverse-burn process. These results demonstrate that the resin/char product has a strong tendency to retain metals. The small amount of metals found in the first trap from the second sample were most likely a result of water which was driven off during the gasification. Some of the water produced recondensed on the char and dripped out of the end of the reactor column. It was included in the first trap solution. This water may have eluted dissolved metal salts. The detection limits for Sr and Cs were

determined to be 0.04 ppm (0.6 % for the traps and 1.2 % for the extract) and 0.3 ppm (0.08 % for the traps and 0.16 % for the extract) respectively.

TABLE 2-4

Percent Recovery of Strontium and Cesium During Reverse-Burn Gasification
of Ion Exchange Resin

Sample Number	Element	Sample Description	% Recovery
1	Sr	Extract	82.0
		Trap 1	0.0
		Trap 2	0.0
	Cs	Extract	97.5
		Trap 1	0.0
		Trap 2	0.0
2	Sr	Extract	82.0
		Trap 1	1.5
		Trap 2	0.0
	Cs	Extract	93.6
		Trap 1	1.3
		Trap 2	0.0

For strontium, the average recovery was 82.8 ± 1.1 %. The average cesium recovery was 96.2 ± 1.8 %. Because the traps contained very little or no metal, it was concluded that the remaining metal probably remained on the char/resin residue as a result of incomplete extraction.

Retention of Radioactive Technetium-99m

The results obtained in the radiotracer experiment are illustrated in Figure 2-4. Activity

is in units of counts/min. The reactor retained 100 % of the radioactivity with 99.9 %
remaining on the char/resin residue. No activity was detected in the char filter. The glass
wool between the char/resin column and the char filter became damp from moisture evolved
during gasification. This moisture probably carried with it the activity that was found on
this glass wool sample. These results demonstrate the superb ability of the char to retain
metals while the organic portion of the waste ion exchange resin is destroyed.
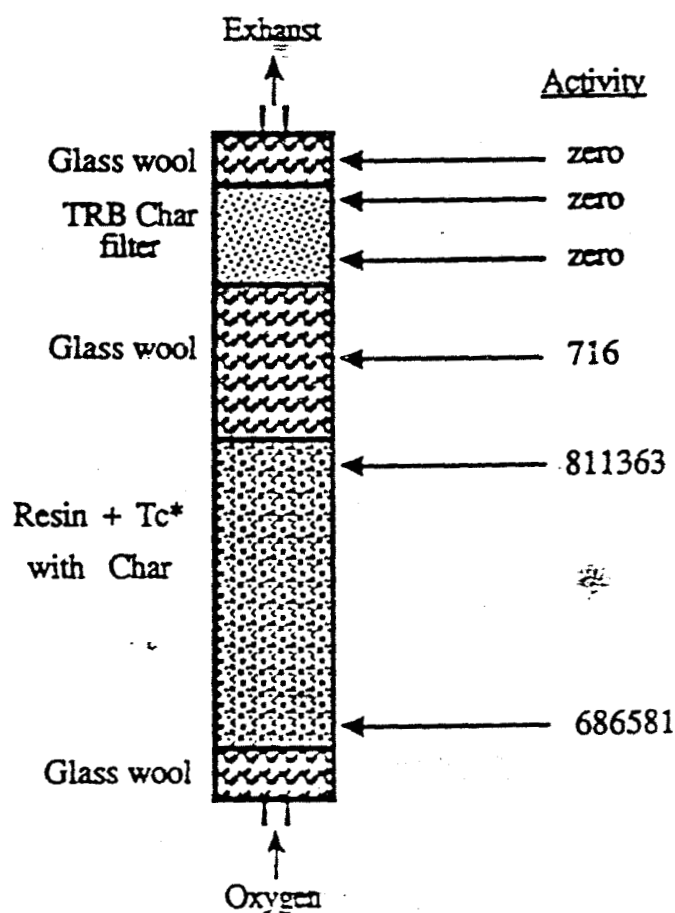
Figure 2-4. Illustration of the reactor used in the technetium study showing the location of
radioactivity after reverse-burn gasification of a resin containing ^{99m}Tc.

Destruction of the Organic Matrix of the Resin and Removal of Water by Reverse-Burn Gasification

Generally, two reverse burns were required to destroy the organics and remove the water. This was determined as illustrated in Figure 2-5, which shows weight loss following multiple reverse burn gasifications. After two passes, the resin/char residue behaved similarly to char alone, which indicated that two reverse burn gasifications were sufficient to remove the water and destroy the organics. The organics were partly gasified and partly carbonized. The mass reduction for the char/resin mixture was 60 % after two reverse burns. Resin accounts for ~60 % of the dry mass of the sample. If the 10 % mass loss for each reverse burn for char is taken into account, there is a net increase in char overall resulting from carbonized resin.
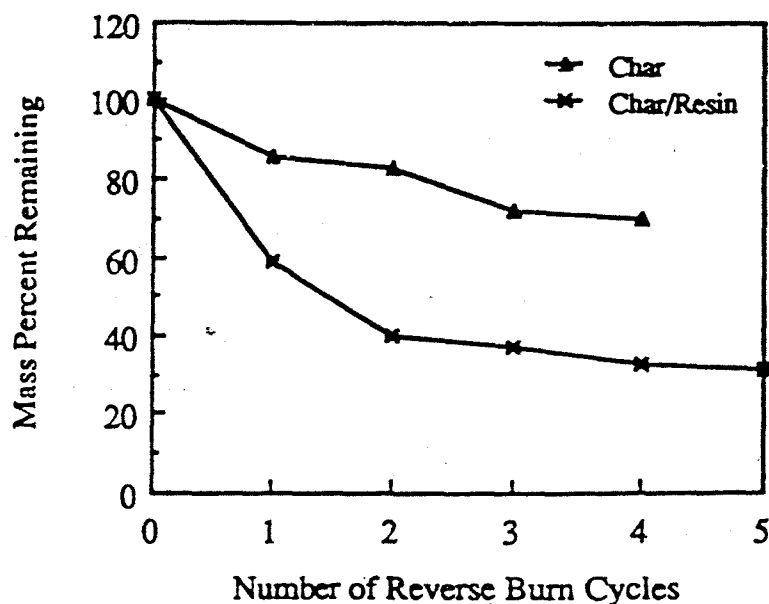
Figure 2-5. Plot of mass loss in reverse burn gasification of char and char/resin mixture.

Surface Analysis of Reverse-Burn Gasification Product

An electron micrograph (SEM) of TRB Char is shown in Figure 2-6. The macroporosity of the TRB Char is evident in its spongy appearance. This property aids in the drying of resin slurries before gasification and may provide a catalytic surface for the thermal destruction of the organic portion of the resin. SEMs of the reverse-burned Amberlite IR-124 resin/char sample are shown in Figures 2-7 and 2-8. Here, the gasified resin/char sample is even more porous than the original char. The surface appears to be very homogeneous indicating that the resin-char interaction during gasification is very intimate. The two substances appear to fuse into one homogeneous char aggregate.

Figure 2-8 is a higher magnification of the same sample shown in Figure 2-7. Deposits can be seen on the surface of the residue. Energy dispersive x-ray analysis (EDAX) performed on the surface to determine the elemental composition of deposits displayed high energy readings for sulfur and sodium. This was not suprising as the resin contained sulfite groups and was in the sodium form for ion exchange. The sulfur may aid in the retention of metals as sulfides in the residue by forming sulfides according to the following reaction:

$$H_2S + M^{2+} \rightarrow MS + 2H^+ \tag{2-1}$$

Recycling of TRB Char/Resin Residue

The average mass reduction for each cycle of reverse-burn gasification was determined to be 47.8 ± 7.3 %. In this experiment, 60 g of wet resin mixed with 6 g TRB Char and 3 g of TRB Char added to facilitate ignition could be reduced to 9.4 g dry char for the first sample and 10 g dry char for the second sample. In general, 60 g wet resin was reduced to 10 g char or less. This was about an 85 % reduction in mass achieved through recycling. No detectable metal was found in any of the trap solutions. This is evidence that the resins

can be reduced completely without loss of metal as vapor.
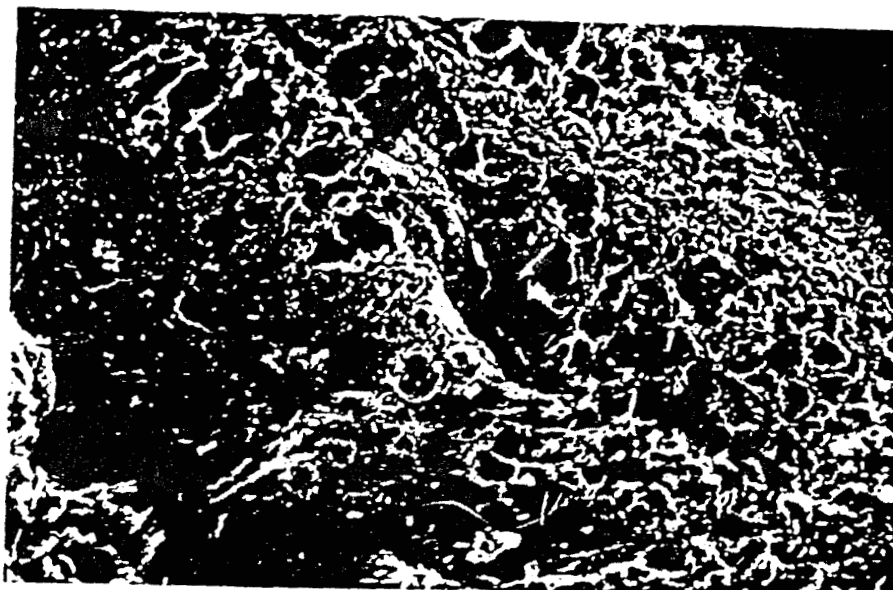

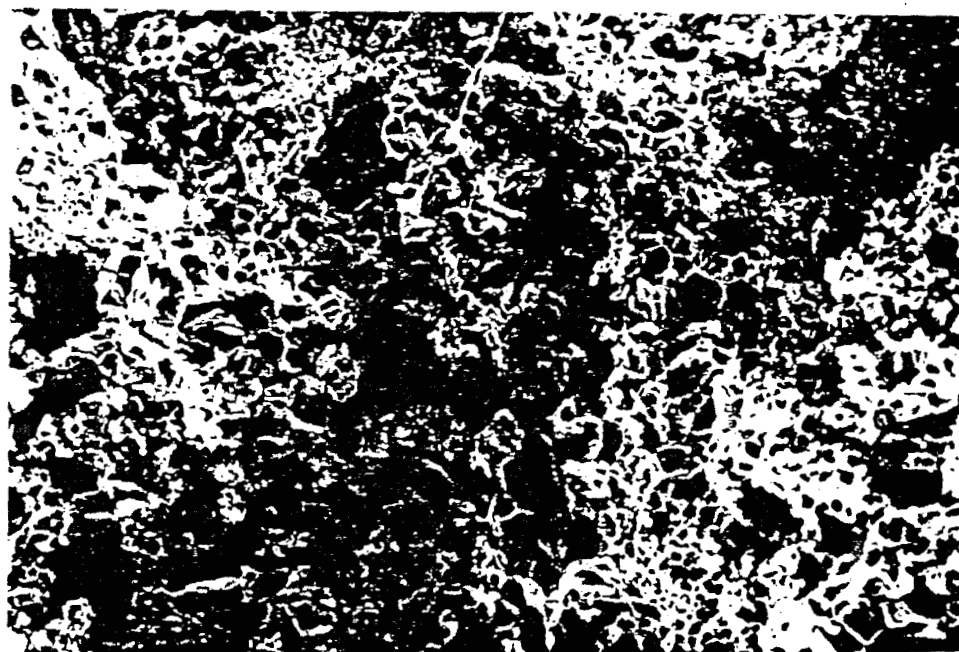Figure 2-6. Scanning electron micrograph of TRB Char at magnification of 150 x.

Figure 2-7. Scanning electron micrograph of Amberlite IR-124/TRB Char mixture reverse-burn gasified one time, magnification of 100 x.
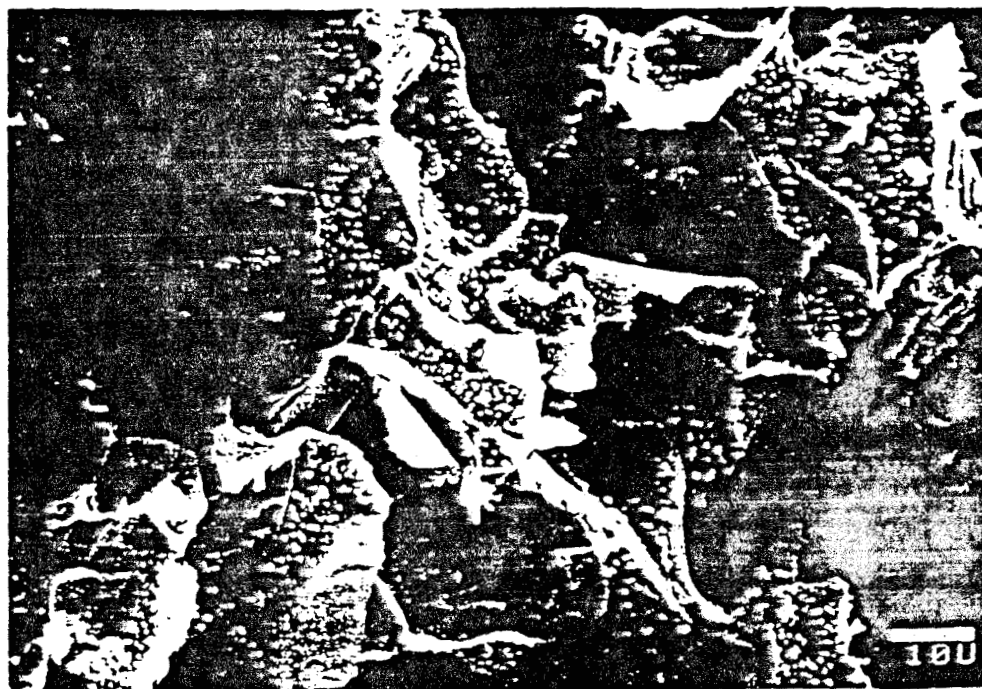
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Figure 2-8. Scanning electron micrograph of Amberlite IR-124/TRB Char mixture reverse-burn gasified one time, magnification of 1000 x.

The duplicate ashed samples gave similar results. After air drying, each sample weighed 14.2 g. After ashing, each weighed 0.4 g. Therefore, 20 g resin plus 6 g TRB Char was reduced to 0.4 g ash. This was 2.8 % of the dry sample weight or, calculating back to wet resin, was 2.0 % of the original mass. A mass reduction of 98 % can be achieved if the resin is converted completely to slag.

Fixation of Gasification Products in Cement

Photographs of the various concrete sample plugs are shown in Figure 2-9 before the were tested to determine the maximum load they could withstand. The resin/cement aggregates formed poor cement products because they were flaky. Pocks from shrunken
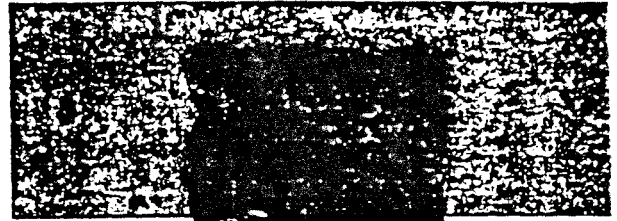
38

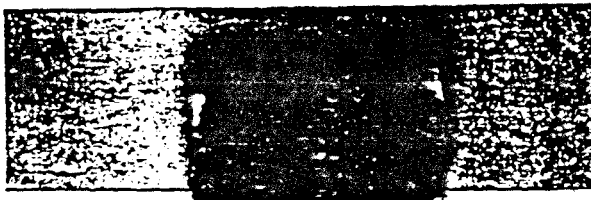Char/Resin Mixture Reverse-Burned Once : Cement (3:1)

Char/Resin Mixture Reverse-Burned Twice : Cement (3:1)

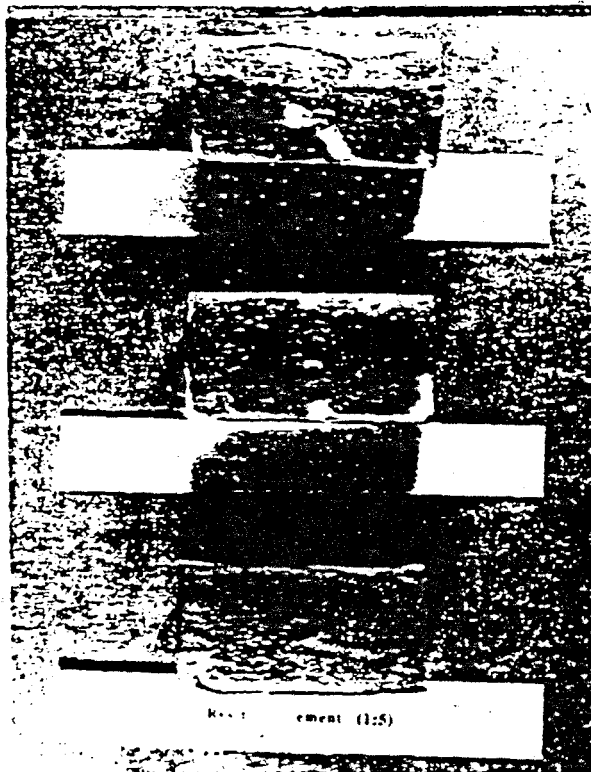Char/Resin Mixture Reverse-Burned Once : Cement (1:1)

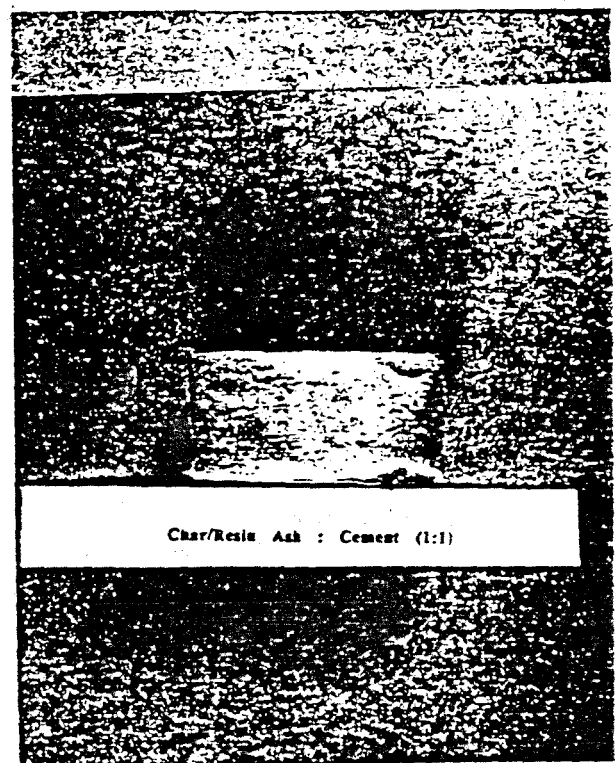Char/Resin Mixture Reverse-Burned Twice : Cement (1:1)

Char Resin Mixture Reverse-Burned Once : Cement (1:3)

Char Resin Mixture Reverse-Burned Twice : Cement (1:3)

Resin : cement (1:5)

Char/Resin Ash : Cement (1:1)

Figure 2-9. Concrete plugs made from resin/cement, char/cement, and ash/cement before testing for compressive strength.

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resin beads are clearly visible on the surface. The ash/cement sample was somewhat powdery. Plugs consisting of gasified resin/char aggregate were homogeneous and porous. Samples containing 3 parts aggregate to 1 part cement were crumbly. The ones with at least 50 % cement mass were easy to handle and relatively hard. The composition and compressive strength for the fixed samples are shown in Table 2-5.

TABLE 2-5

Composition and Compressive Strength of Resin, Char, and Portland Cement Mixtures

| Sample number	Aggregate mass (g)	Cement mass (g)	Cement: aggregate	Percent aggregate	Maximum load (lb)	Maximum load (psi)
Resin aggregate						
1	6.0	30.0	1:5	16.7	980	770
2	3.0	30.0	1:10	9.1	2257	1773
3	1.5	30.0	1:20	4.8	2752	2142
Char/resin mixture reverse-burned once						
4	12.0	36.0	1:3	25	668	525
5	16.0	16.0	1:1	50	255	200
6	21.0	7.0	3:1	75	10	7.9
Char/resin mixture reverse-burned twice						
7	12.0	36.0	1:3	25	441	346
8	16.0	16.0	1:1	50	178	140
9	21.0	7.0	3:1	75	6	4.7
Char/resin mixture gasified with one reverse-burn, then forward-burned to ash						
10	16.4	16.4	1:1	50	134	105
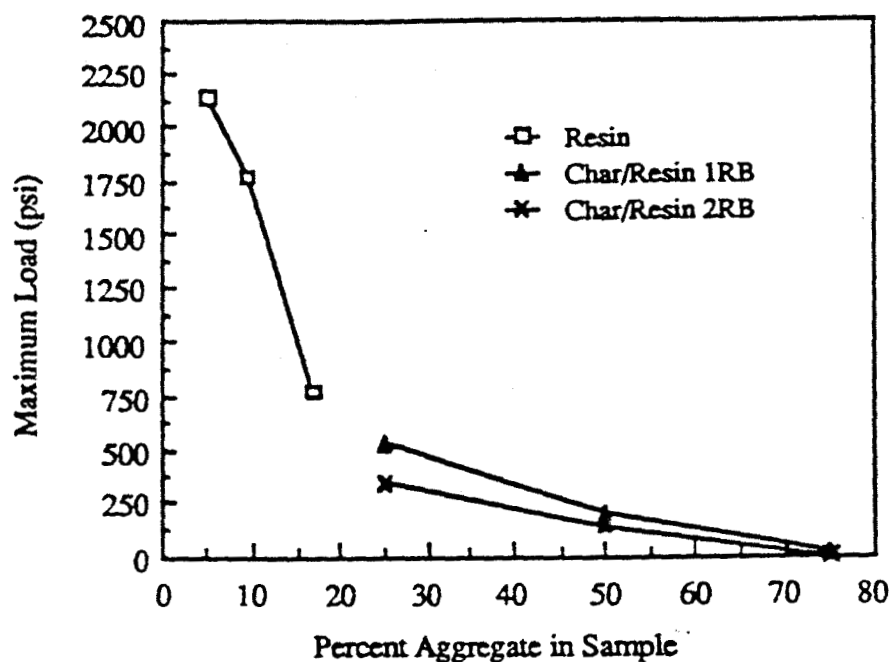
Figure 2-10. Plot of strength of cement aggregates versus composition.

Leachability of the Final Cement Product

The results of the leaching study are shown in Table 2-6 which lists the results obtained in the ICP-AES analysis. The percent metal leached (Table 2-7) was estimated by calculating the total mg metal in the 600 mL leachate and dividing by the total metal added to the resin in the sample. The amount of Fe and Zn in the water blank was subtracted from the result obtained for those elements. The amount of metal leached appeared to be related to the particular sample and not to a particular metal.

The values for metals leached were all less than 1 % except for the third sample which showed slightly greater than 1 % leaching for iron, manganese, and zinc. Sample 5 also leached slightly more than samples 1, 2 and 4. The reason for the variation in samples 3 and 5 was not determined. This EPA test is designed to simulate sanitary landfill leaching

for eight elements, four pesticides, and two herbicides. Chromium is the only element of the group tested in this study. The leaching of chromium was below that for the blank sample. The waste is considered non-hazardous unless the extract exceeds that specified in 40 CFR 261.24.

TABLE 2-6

ICP-AES Results of Leaching Study (ppm)

Sample	Cobalt	Chromium	Iron	Manganese	Zinc
1	<0.01	0.040	0.20	0.006	0.052
2	<0.01	0.03	0.043	0.015	0.021
3	0.02	0.02	0.10	0.035	0.041
4	<0.01	0.02	0.029	0.014	0.014
5	0.02	0.02	0.039	0.031	0.034
blank	<0.01	0.085	0.030	0.006	0.006
water blank	<0.01	<0.01	0.01	<0.003	0.003
Limit of detection	0.01	0.01	0.005	0.003	0.002

TABLE 2-7

Estimate of Percent Metal Leached from Concrete Samples

Sample	Cobalt	Chromium	Iron	Manganese	Zinc
1	--	0.8	0.2	0.12	0.98
2	--	0.6	0.66	0.3	0.36
3	0.6	0.6	2.7	1.05	1.14
4	--	0.6	0.57	0.42	0.33
5	0.6	0.6	0.87	0.93	0.93

CONCLUSIONS

It has been demonstrated that coal char can be used successfully to treat waste organic ion exchange resins. The treatment consists of several simple steps in which the organic matrix of the resin is destroyed leaving a dry inorganic residue or slag that can readily be fixed in cement. The waste is no longer considered a mixed waste because the organic component has been destroyed and it can be handled under existing regulations.

The gases given off during reverse-burn gasification depend upon the specific resin(s) being treated and upon the operating parameters. The primary vapor phase products are H_2O, CO, and CO_2. In smaller amounts, nitrogen products, such as NH_3, are obtained from anion resins and sulfur products, such as H_2S and elemental sulfur vapor, are obtained from cation resins.

The dried resin could be gasified alone, without pre-mixing with char. This produced copious amounts of sulfur gases which could be filtered through a plug of char. On a laboratory scale, however, the process appears to be optimized by mixing spent resin slurry with dry char in a 10:3 ratio by weight. After the mixture has been allowed to dry to remove excess water, it can be processed through two reverse burn gasification cycles and the product then mixed with an additional 10 parts of spent resin slurry. The entire cycle can be repeated one or more times, and the product set in cement. The concrete products formed by mixing 50 % by mass cement with char or ash exceed the accepted 50 psi compressive strength minimum.

The calculations discussed above are summarized in Figure 2-11. The volume considerations discussed above are based on an assumed 50 % loading in cement. The excellent aggregate properties of the char/slag mass leads to a good quality cement product. Furthermore, the presence of activated carbon in the product is an added feature that retards leaching.

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This research has demonstrated on a laboratory scale that, starting with a high-moisture, mechanically-weak, organic resin matrix that is susceptible to radiolytic damage, the reverse-burn process can produce an inert, dry, leach-resistant disposal form in a carbon/mineral matrix. Therefore, the process is highly effective for the stabilization, solidification, and volume reduction of spent organic resins used for the treatment of low level radioactive liquid waste.
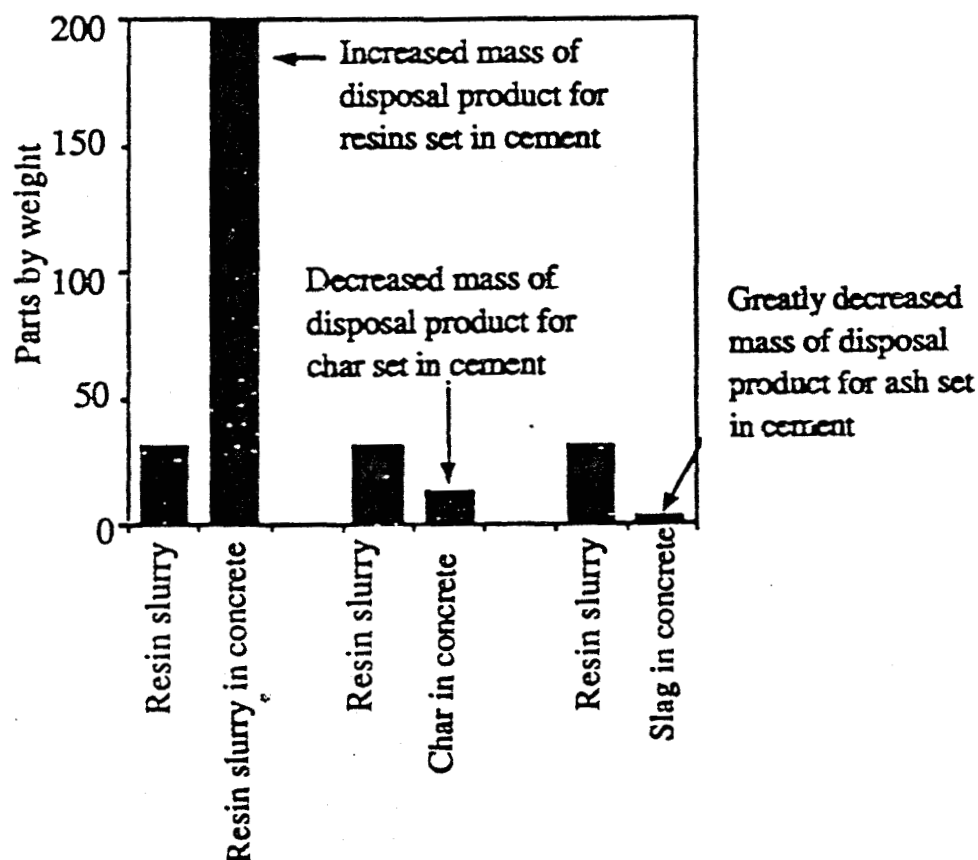

Figure 2-11. Relative masses of resin slurry and final disposal forms for various disposal options.

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Procedures have been developed that enable mixing the char and resin slurry together in a uniform mixture that dries and handles readily. Retention to an extent of 98.5–100.0 % has been demonstrated for cesium and strontium bound to cation exchange resins. Complete retention (100.0 %) in a char matrix has been demonstrated for radioactive technetium-99m sorbed to an anion exchange resin. Fly ash produced in the forward-burn mode can be removed from the effluent by filtering with char.